Gas/Surface Interaction Models for Porous Media

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Acknowledgments
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Outline

- Motivation
- Porous Microstructure Analysis (PuMA)
- Surface chemistry framework in PuMA
- GS and PS reactions
- Molecular beam experiments
- Vitreous Carbon (VC) model
- Extension of VC model to FiberForm®
- Effective model for use in CFD
- Summary/Future Work

Motivation

Image credit: NASA

Reusable TPS material considerations: catalycity, emissivity, toughness

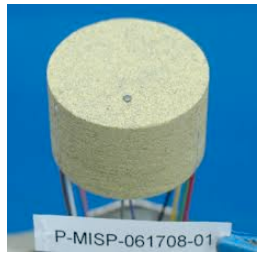


Image credit: NASA

Ablative TPS material considerations: recession, oxidation, pyrolysis

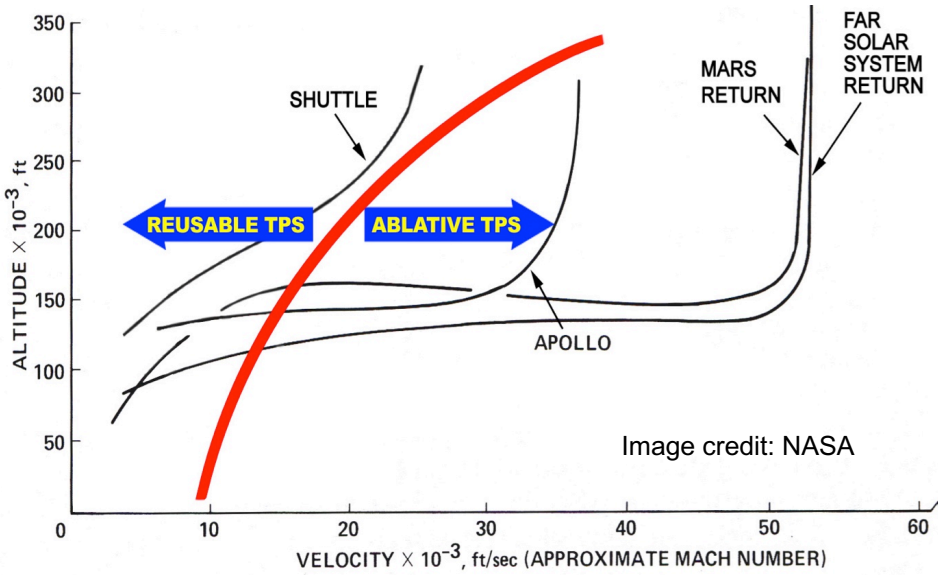


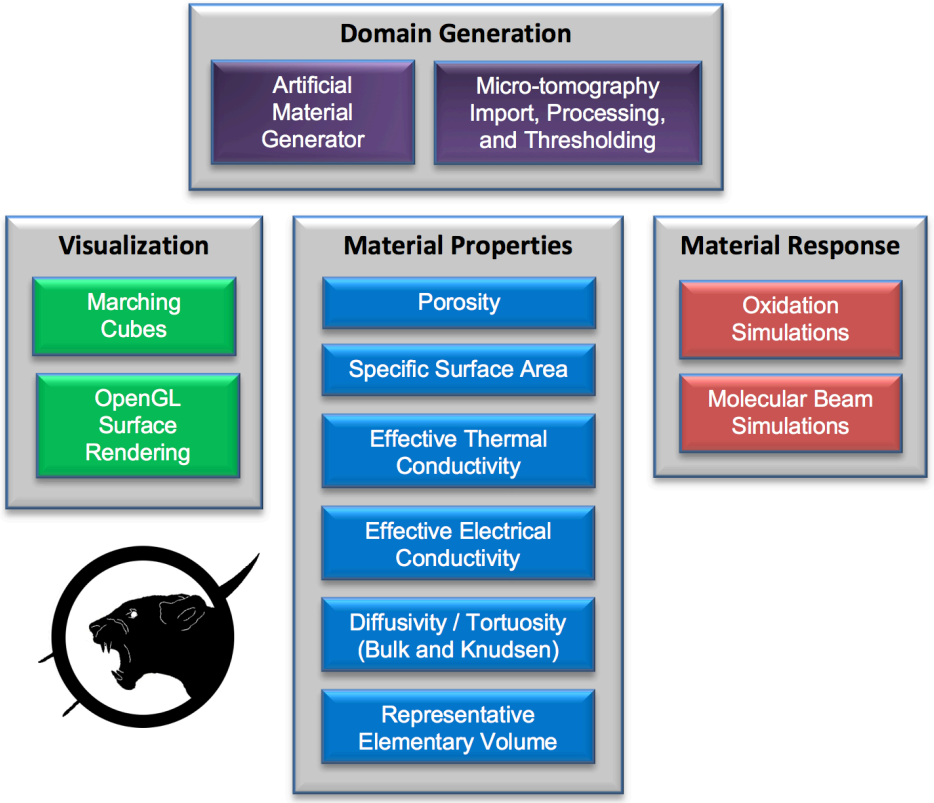
Image credit: NASA

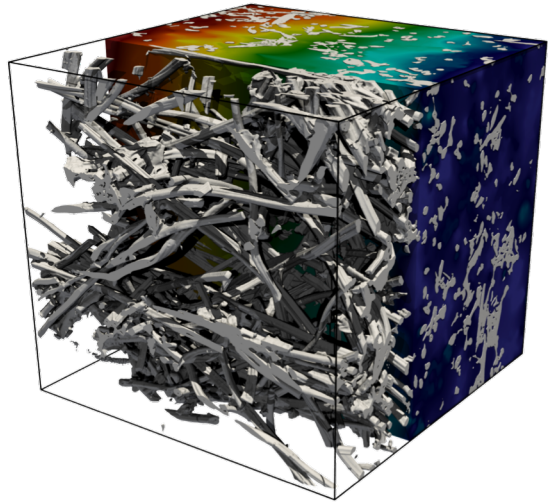
Objectives:

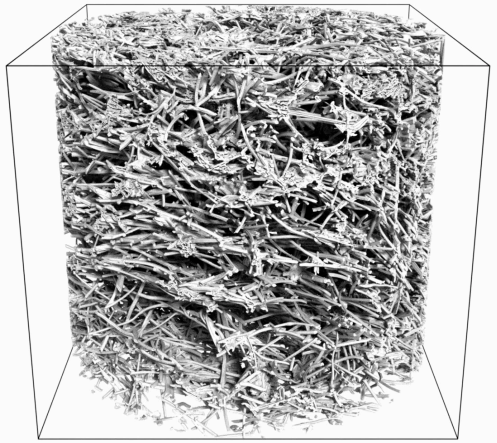
- Characterize carbon surface recession/ablation due to oxidation
- Develop a predictive model of carbon oxidation for use in CFD/DSMC/material response

Porous Microstructure Analysis (PuMA) [1]

Porous Microstructure Analysis (PuMA)



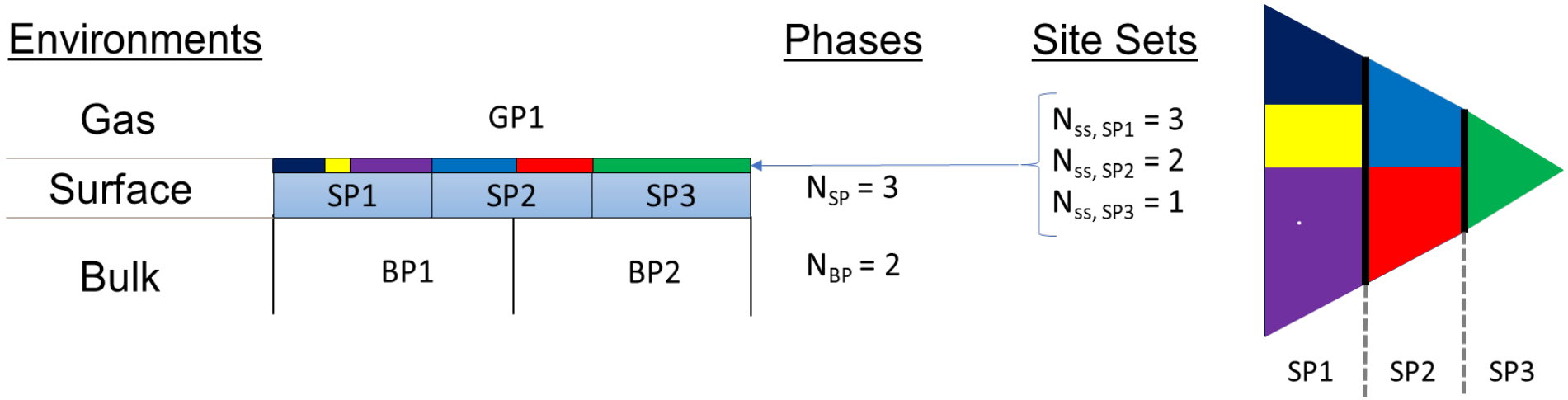




[1] J. C. Ferguson, F. Panerai, A. Borner, N. N. Mansour, ***PuMA: the Porous Microstructure Analysis software***, SoftwareX 7 (2018) 81–87.

Surface chemistry framework in PuMA

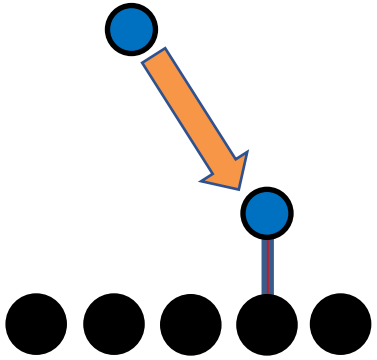
- Methodology to represent surface sites similar to Marschall, Maclean and Driver [2] for CFD.
- Particles adsorbed (deleted) and desorbed (created), surface element stores adsorbed particle concentration.
- Surface reactions based on concentration within surface element.
- Multiple triangulated elements (like cells) on surfaces
- Langmuir model for surface sites.



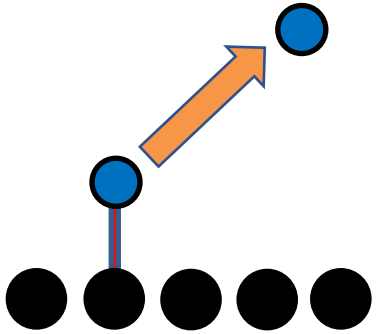
[2] Marschall, J., & MacLean, M. (2011). Finite-rate surface chemistry model, I: Formulation and reaction system examples. AIAA Paper, 3783, 2011.

Surface Reaction Mechanisms

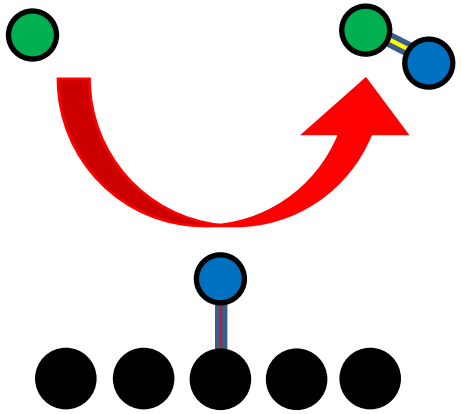
Adsorption



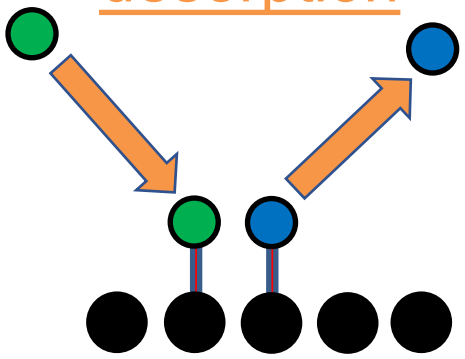
Desorption



Eley-Rideal

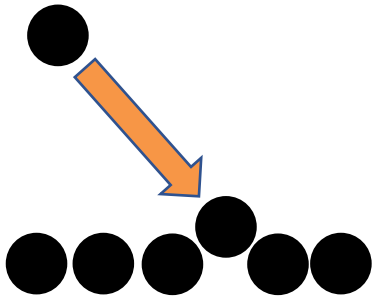


Collision-induced desorption

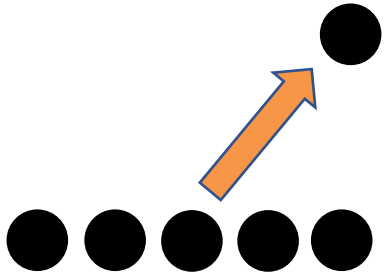


Surface Reaction Mechanisms

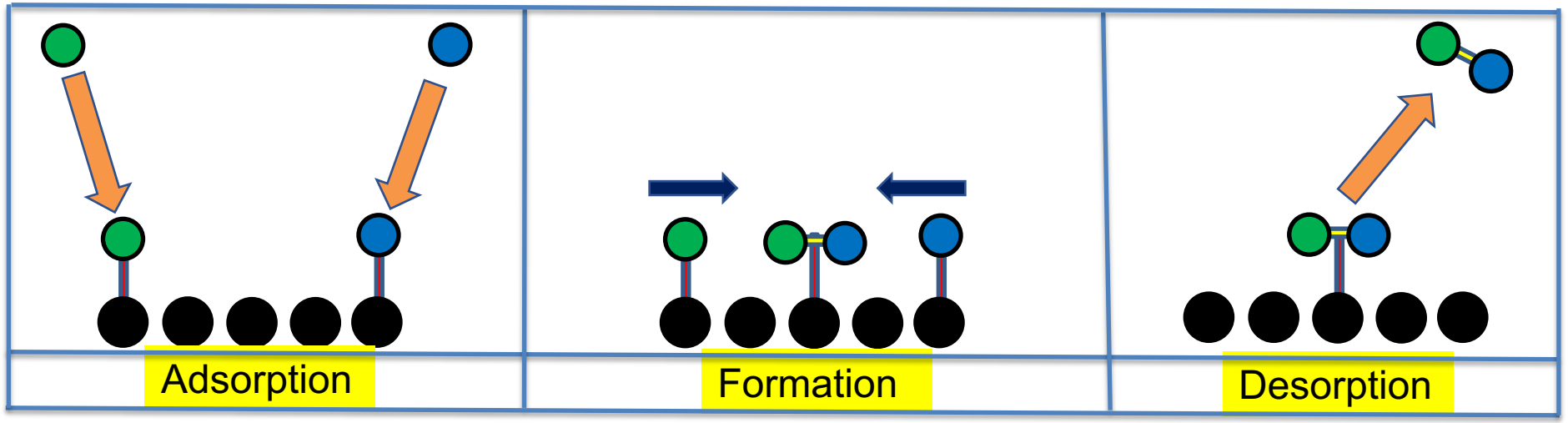
Condensation



Sublimation



Langmuir-Hinshelwood



Different Types of LH Mechanisms

The Langmuir-Hinshelwood mechanism has two steps – Formation
Desorption

$$O(g) + (s) \rightarrow O(s)$$
$$O(s) + C(b) \rightarrow CO(s) \quad (1) - t_f$$
$$CO(s) \rightarrow CO(g) + (s) \quad (2) - t_d$$

$$O(g) + C(b) \rightarrow CO(g) \quad (3)$$

$O(s)$ – Reactant
$CO(s)$ – Intermediate
$CO(g)$ – Product

Time scale of interest = τ

Based on time scale arguments 4 types of LH mechanisms can be defined

1. $t_f << \tau$ $t_d << \tau$ - Prompt thermal mechanism
2. $t_f \sim \tau$ $t_d << \tau$ - LH limited by formation
3. $t_f << \tau$ $t_d \sim \tau$ - LH limited by desorption
4. $t_f \sim \tau$ $t_d \sim \tau$ - LH limited by both desorption and formation

List of gas-surface (GS) reactions

- Reactants include both gas-phase and surface species.
- Comprehensive set of reactions – Includes reaction types from thermal regime and hyperthermal energy regime.

Symbol	Reaction type	Examples
1: AA	Associative Adsorption	$O(g) + (s) \longrightarrow O(s)$ $O_2(g) + (s) \longrightarrow O_2(s)$
2: DA	Dissociative Adsorption	$O_2(g) + (s) \longrightarrow O(s) + O(g)$ $O_2(g) + 2(s) \longrightarrow 2O(s)$
3: DIS	Dissociation	$O_2(g) + (s) \longrightarrow 2O(g) + (s)$ $CO_2(g) + (s) \longrightarrow 2O(g) + (s) + C(b)$
4: LH1	Langmuir-Hinshelwood type 1	$O(g) + (s) + O(s) \longrightarrow O_2(g) + 2(s)$ $O(g) + (s) + C(b) \longrightarrow CO(g) + (s)$
5: LH3	Langmuir-Hinshelwood type 3	$O(g) + (s) + O(s) \longrightarrow O_2(s) + 2(s)$ $O(g) + (s) + C(b) \longrightarrow CO(s) + (s)$
6: CD	Condensation	$C_3(g) + 3(s) \longrightarrow 3C(b) + 3(s)$
7: ER	Eley-Rideal	$CO(g) + O(s) \longrightarrow CO_2(g) + (s)$
8: CI	Collision Induced	$O(g) + CO(s) \longrightarrow CO(g) + O(s)$ $Ar(g) + O(s) \longrightarrow Ar(g) + O(g) + (s)$

Modeling of gas-surface (GS) reactions

- GS reaction probability computed when gas-phase species hits surface.
- Reaction probability function of:
  - rate constant
  - gas-phase particle properties (energy, angle, etc.)
  - surface conditions (temperature, surface coverage, etc.)

Reaction type	Sample	Probability
Adsorption	$A(g) + (s) \longrightarrow A(s)$ $A_2(g) + (s) \longrightarrow 2A(s)$	$P = S^{\alpha}(\theta) = f(S_0, \theta, \alpha)$ [3]
Adsorption mediated reactions: Dissociation, LH1, LH3, Condensation	$A_2(g) + (s) \longrightarrow 2A(g) + (s)$ $A(g) + (s) + B(s) \longrightarrow AB(g) + 2(s)$	$P = P_{ad} * k_{reac}$ $P = P_{ad} * k_{reac} * \frac{N_{B(s)} F_N}{S_p}$
Eley-Rideal	$A(g) + B(s) \longrightarrow AB(g) + (s)$	$P = 2k_{reac} \frac{N_{B(s)} F_N}{S_p} \frac{1}{v_n}$ [4]
Collision Induced	$A(g) + B(s) \longrightarrow A(g) + B(g) + (s)$	$P = k_{reac} \frac{N_{B(s)} F_N}{S_p} (E_{in})^m \cos^n(\theta)$ [5]

[3] Kisliuk, P. "The sticking probabilities of gases chemisorbed on the surfaces of solids." JPhysChemSolids 3, no. 1-2 (1957): 95-101
[4] Molchanova, *et al*. "A detailed DSMC surface chemistry model." In AIP Conference Proceedings, vol. 1628, no. 1, pp. 131-138. AIP, 2014.
[5] Rettner and Lee. "Dynamic displacement of O2 from Pt (111): A new desorption mechanism." The JChemPhys 101, no. 11 (1994):

List of pure-surface (PS) reactions

- Pure-surface (PS) reactants include only surface species (adsorbed and bulk).
- Comprehensive set of reactions

Symbol	Reaction type	Examples
1: DS	Desorption	$O(s) \longrightarrow O(g) + (s)$ $O_2(s) \longrightarrow O_2(g) + (s)$
2: LH2	Langmuir-Hinshelwood type 2	$N(s) + O(s) \longrightarrow NO(g) + 2(s)$ $O(s) + C(b) \longrightarrow CO(g) + (s)$
3: LH4	Langmuir-Hinshelwood type 4	$N(s) + O(s) \longrightarrow NO(s) + (s)$ $O(s) + C(b) \longrightarrow CO(s) + (s)$
4: SB	Sublimation	$3C(b) + 3(s) \longrightarrow C_3(g) + 3(s)$

Modeling of pure-surface (PS) reactions

- Characteristic time computed between two reactions: Time counter method [5].
- Characteristic time function of
  - reaction rate constant
  - surface conditions (temperature, surface coverage, etc.).

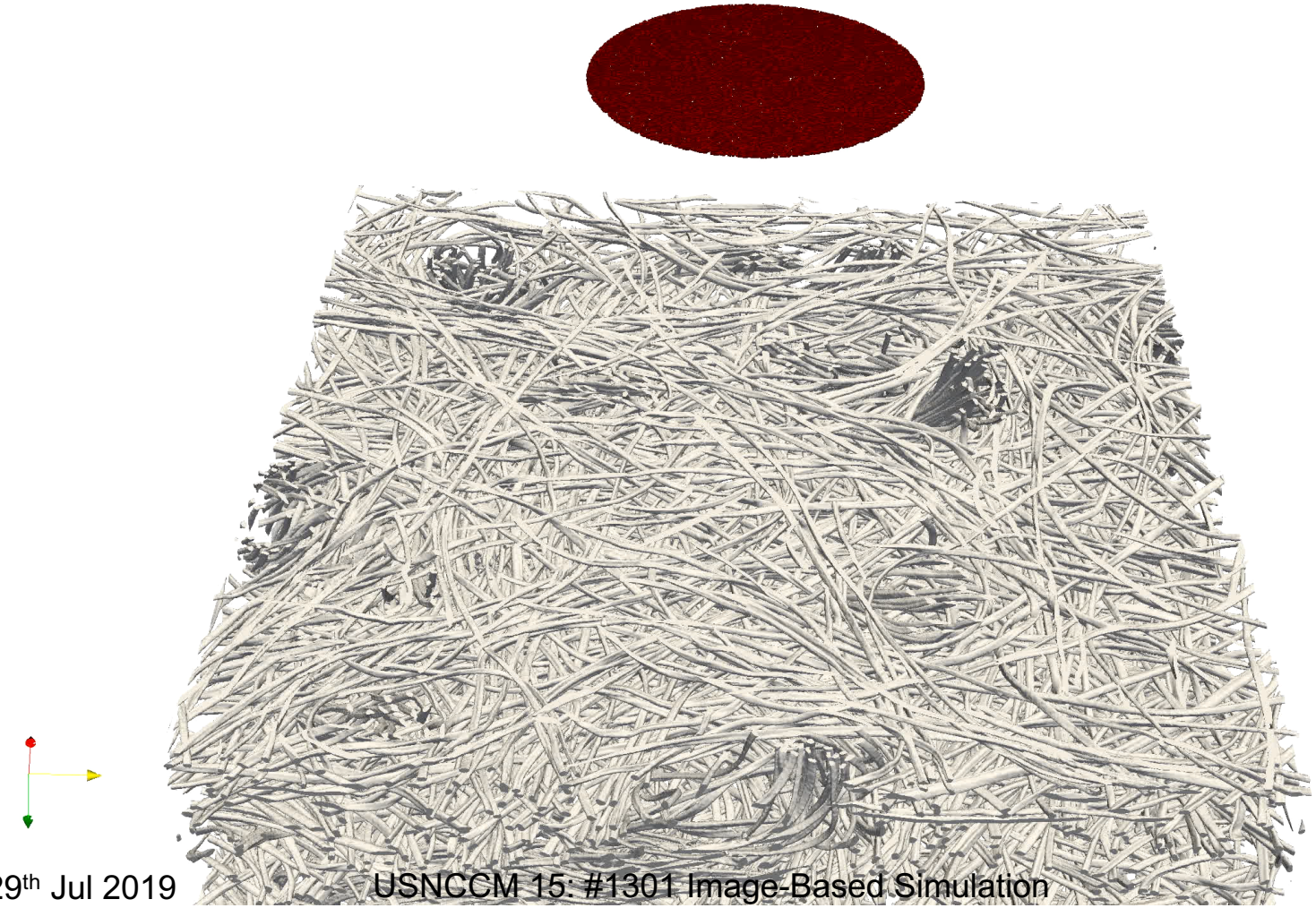
$$\tau_{reac} = \frac{-log(Rn)}{\nu_{reac}}$$

- Time counter algorithms developed to be independent of dt.

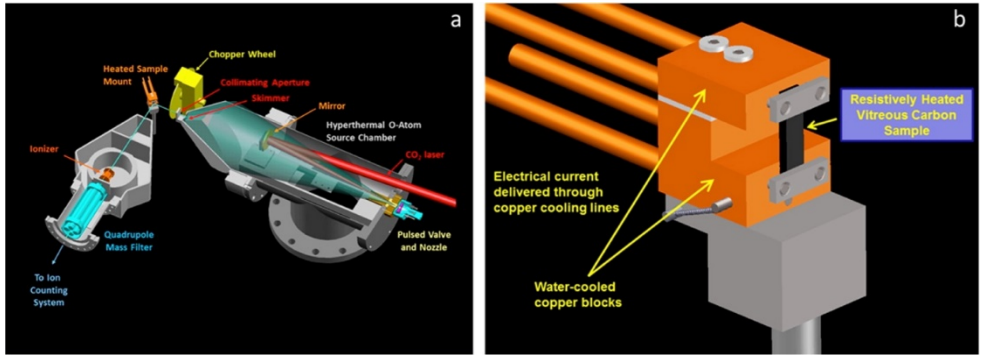
Reaction type	Sample	Frequency
Desorption Sublimation	$A(s) \longrightarrow A(g) + (s)$	$\frac{dn_{A(s)}}{dt} = -k_{reac} n_{A(s)}$ $\nu_{reac} = k_{reac} N_{A(s)}$ [4]
LH-2, LH-4	$A(s) + B(s) \longrightarrow AB(g) + 2(s)$	$\frac{dn_{A(s)}}{dt} = \frac{dn_{B(s)}}{dt} = -k_{reac} n_{A(s)} n_{B(s)}$ $\nu_{reac} = k_{reac} N_{A(s)} N_{B(s)} \frac{F_N}{S_p}$

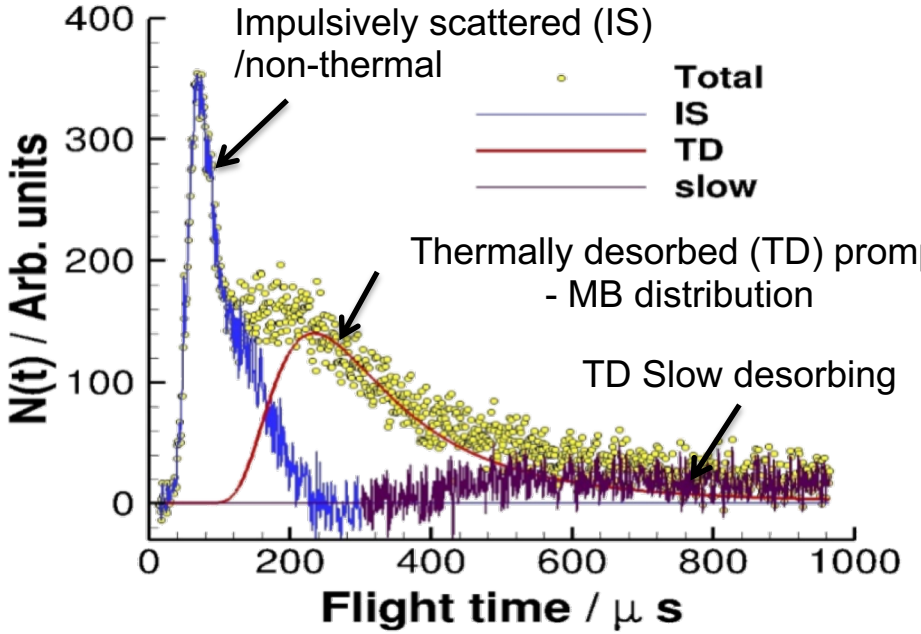
[4] Molchanova, A. N., A. V. Kashkovsky, and Ye A. Bondar. "A detailed DSMC surface chemistry model." In AIP Conference Proceedings, vol. 1628, no. 1, pp. 131-138. AIP, 2014.

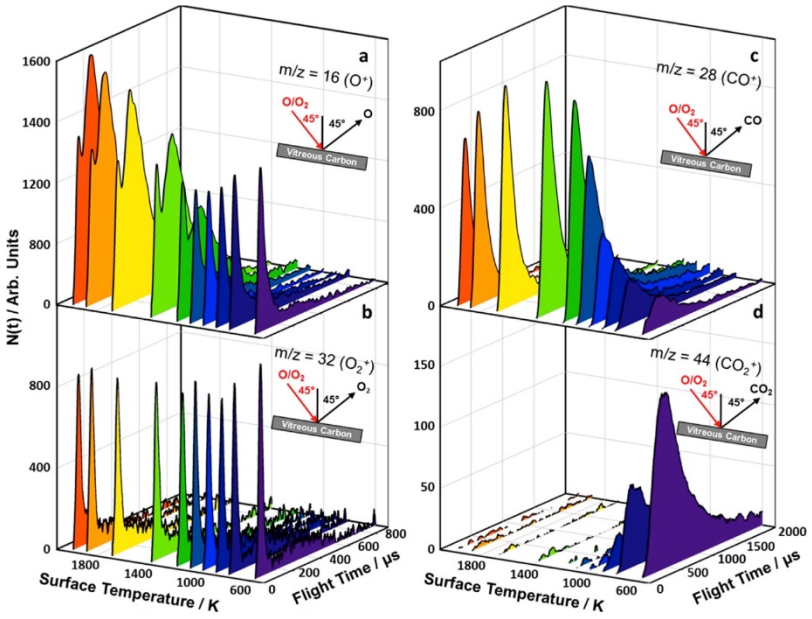
Reactive scattering simulation in PuMA

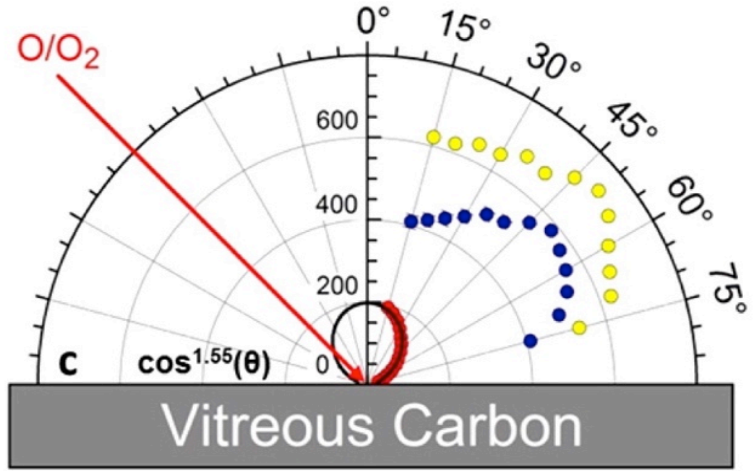


Molecular Beam Experimental Setup [6]









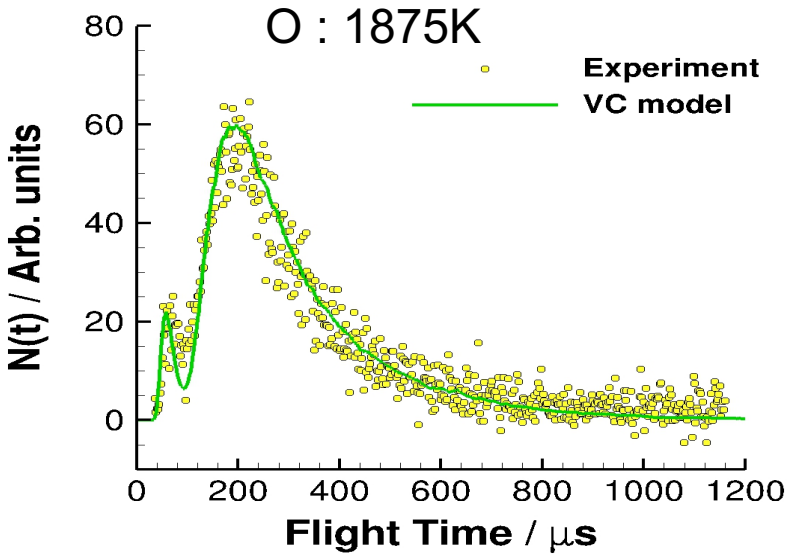
Reprinted with permission from "[6] Murray, V J., et al. *The Journal of Physical Chemistry C* 119.26 (2015): 14780-14796. Copyright 2015. American Chemical Society.

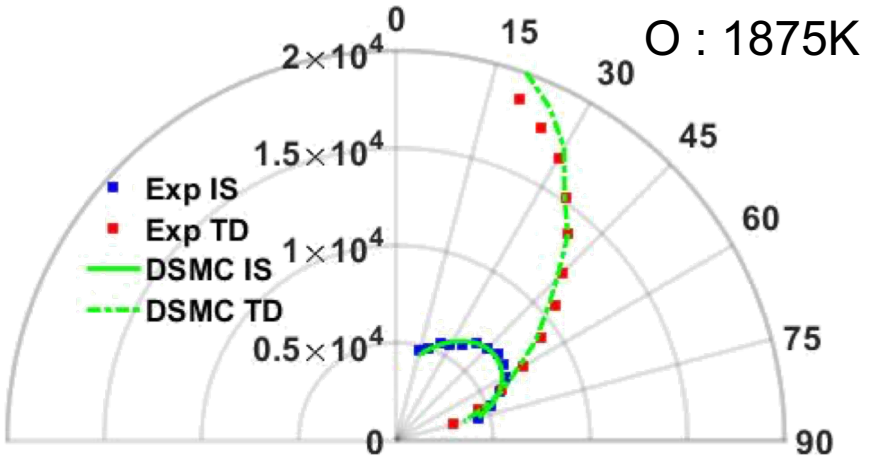
Vitreous Carbon (VC) Oxidation Model [7]

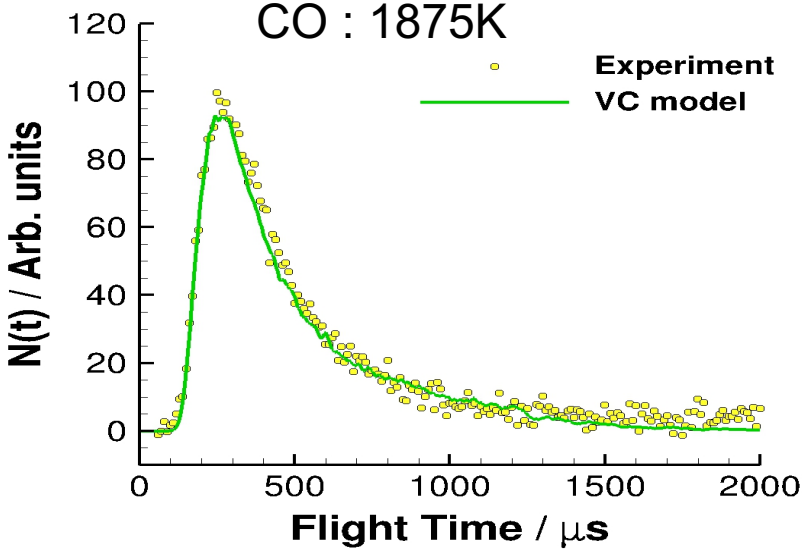
Type	Mechanisms	Reaction	Rate constant (k)
Adsorption	Adsorption	$O(g) + (s) \longrightarrow O(ads)$	$\frac{1}{\Phi} * \frac{1}{4}\sqrt{\frac{8k_bT_g}{\pi m}} * 0.85$
Adsorption-mediated GS reactions	LH1 O formation	$O(ads) \longrightarrow O(TD)(g) + (s)$	$20.9\ exp(-\frac{2449.3}{T_s})$
	LH1 CO formation	$O(ads) + C(b) + O'(ads) \longrightarrow CO(g) + (s) + O'(ads)$	$\frac{1}{\Phi} * 1574.9\ exp(-\frac{6240.0}{T_s})$
	LH1 CO_2 formation	$O(ads)+O(s)+C(b)+4O'(ads) \longrightarrow CO_2(g)+2(s)+4O'(ads)$	$\frac{1}{\Phi^5} * 536.3\ exp(-\frac{655.6}{T_s})$
	LH3 O{a} formation	$O(ads) \longrightarrow O\{a\}(s)$	1
	LH3 CO{a} formation	$O(ads) + C(b) + O'(ads) \longrightarrow CO\{a\}(s) + O'(ads)$	$\frac{1}{\Phi} * 153.0\ exp(-\frac{4172.8}{T_s})$
	LH3 CO{b} formation	$O(ads) + C(b) + O'(ads) \longrightarrow CO\{b\}(s) + O'(ads)$	$\frac{1}{\Phi} * 71.2\ exp(-\frac{1161.2}{T_s})$
PS reactions	LH3 O{a} desorption	$O\{a\}(s) \longrightarrow O(g) + (s)$	$0.050457\ T^2\ exp\left(-\frac{3177.2}{T_s}\right)$
	LH3 CO{a} desorption	$CO\{a\}(s) \longrightarrow CO(g) + (s)$	$4485.5\ exp\left(-\frac{1581.4}{T_s}\right)$
	LH3 CO{b} desorption	$CO\{b\}(s) \longrightarrow CO(g) + (s)$	$1.2194\ exp\left(-\frac{2251.6}{T_s}\right)$

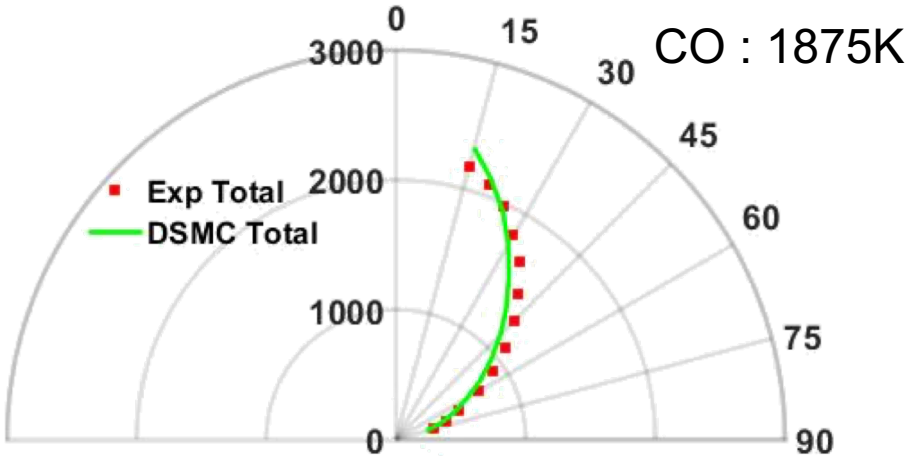
[7] K. Swaminathan-Gopalan *et al.*, "***Development and validation of a finite-rate model for carbon oxidation by atomic oxygen***." Carbon 137 (2018): 313-332.

Vitreous Carbon (VC) Oxidation Model

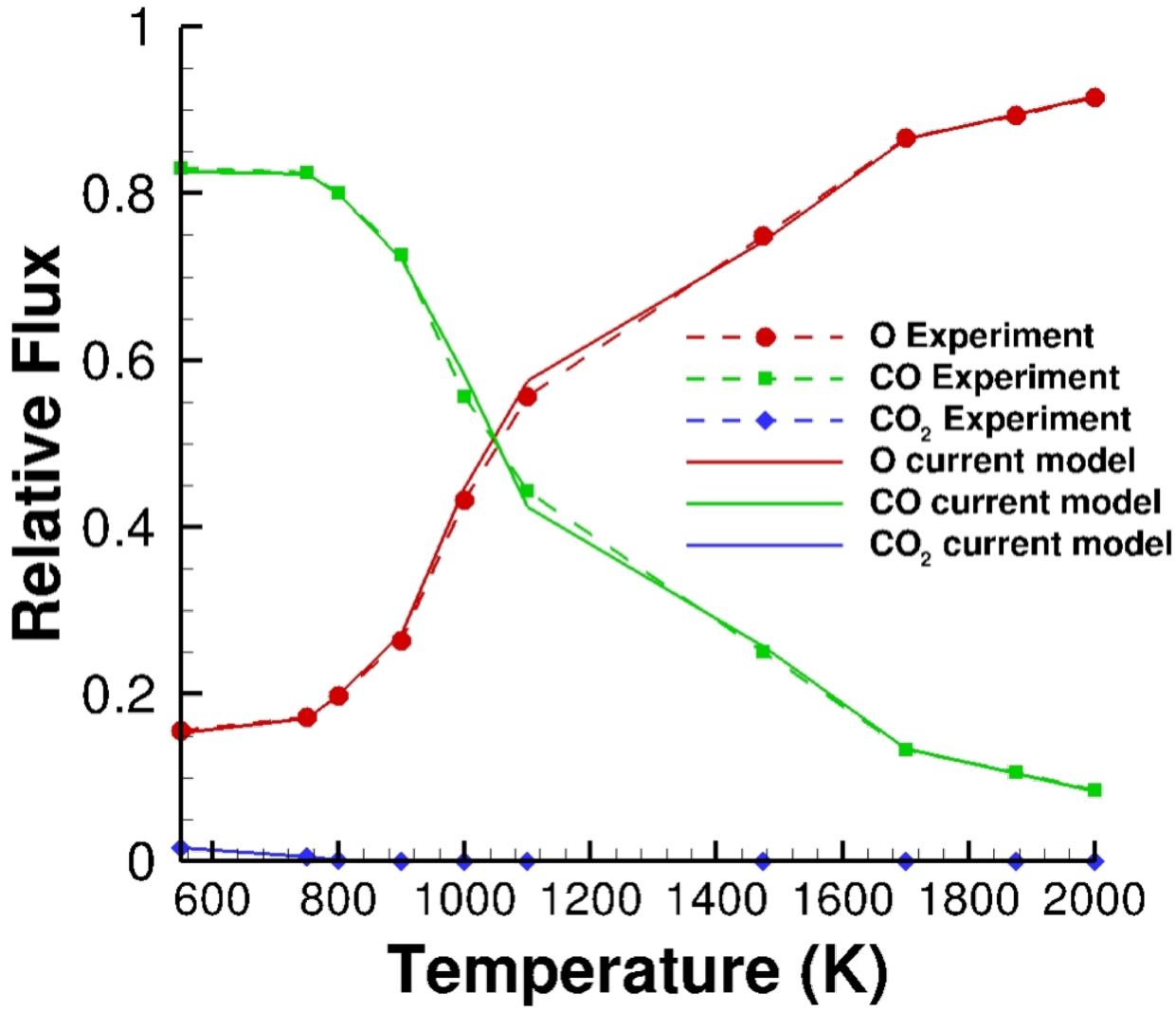








Vitreous Carbon (VC) Oxidation Model



Effective models for use in CFD: Extension of VC model to FiberForm®

Objectives:

- **Develop a predictive model of carbon oxidation for use in CFD**

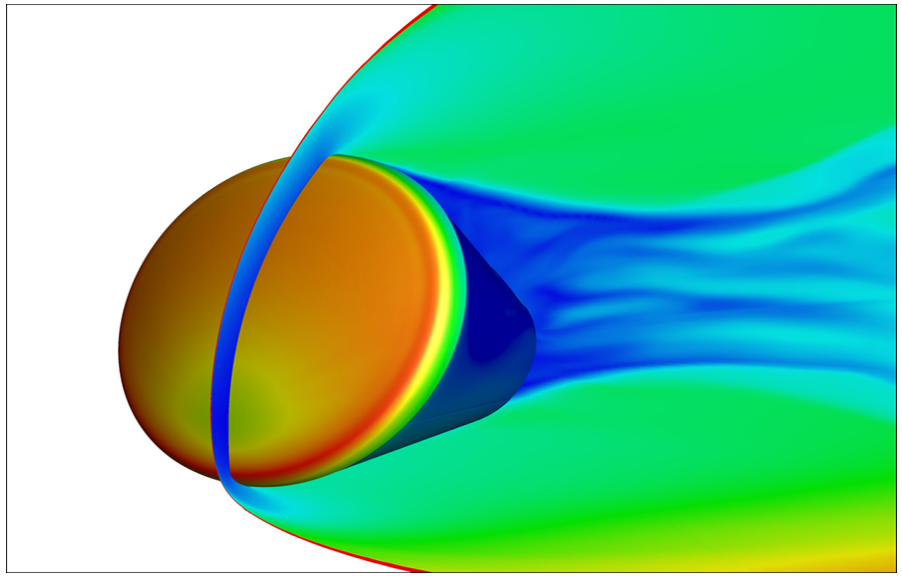
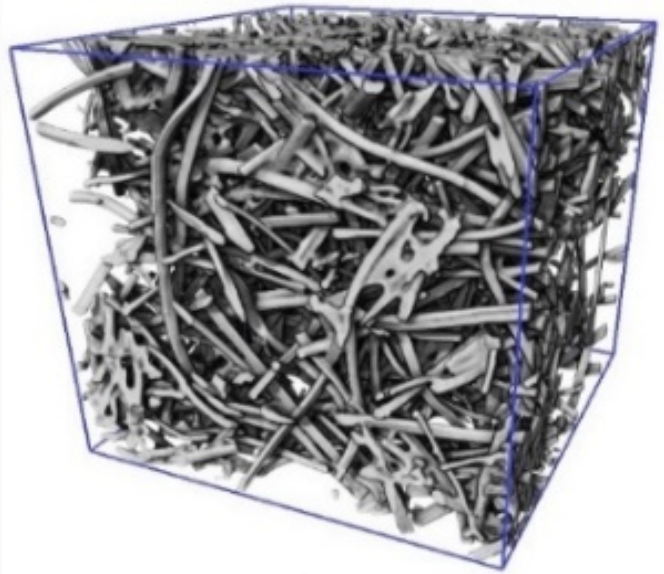
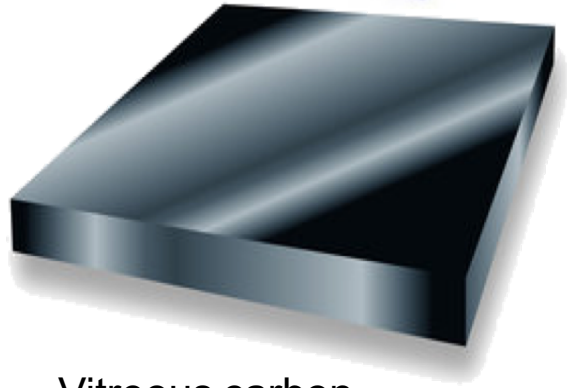


Image credit: NASA

FiberForm®





Vitreous carbon

Artist rendering.
Credit: SPI Supplies Division of Structure Probe, Inc

Effective model for use in CFD

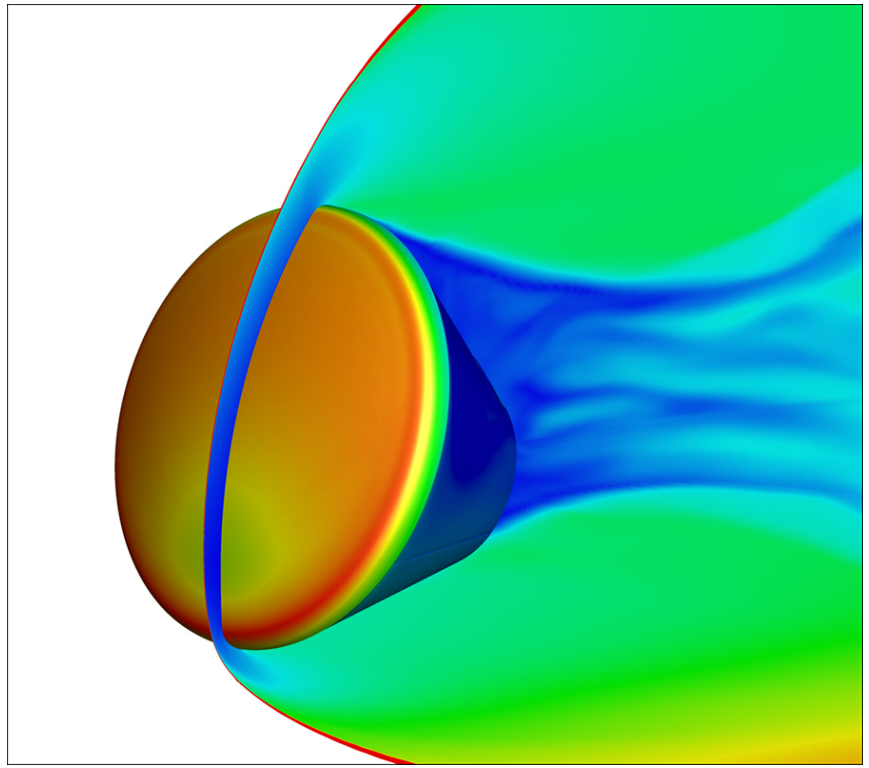
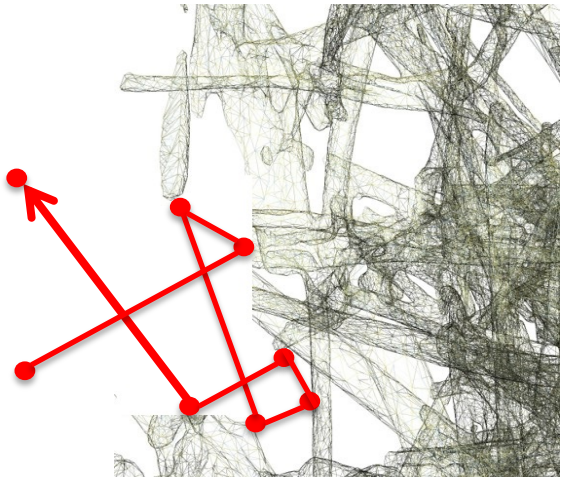
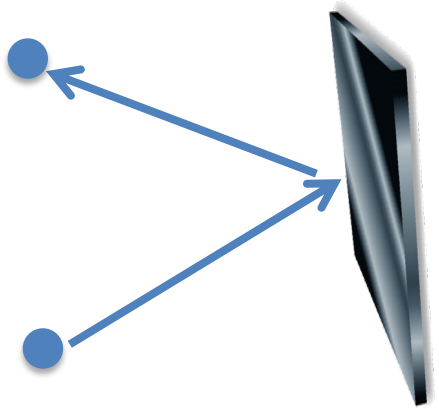


Image credit: NASA



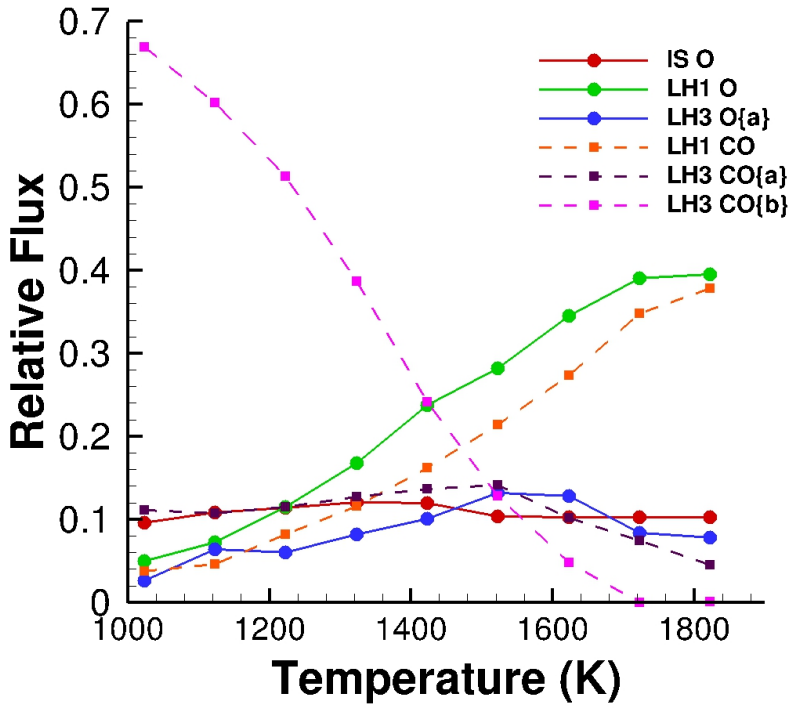
Real model
Rates → k



Effective model
Rates → k_{eff}

Effective model for use in CFD

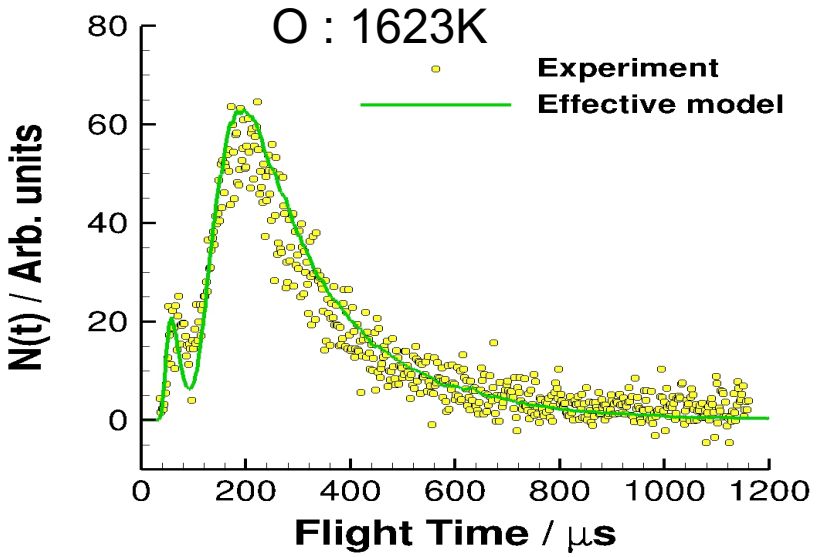
Type	Mechanisms	Reaction
Adsorption	Adsorption	$O(g) + (s) \longrightarrow O(ads)$
GS reactions	LH1 O formation	$O(ads) \longrightarrow O(TD)(g) + (s)$
	LH1 CO formation	$O(ads) + C(b) + O'(ads) \longrightarrow CO(g) + (s) + O'(ads)$
	LH3 O{a} formation	$O(ads) \longrightarrow O\{a\}(s)$
	LH3 CO{a} formation	$O(ads) + C(b) + O'(ads) \longrightarrow CO\{a\}(s) + O'(ads)$
	LH3 CO{b} formation	$O(ads) + C(b) + O'(ads) \longrightarrow CO\{b\}(s) + O'(ads)$
PS reactions	LH3 O{a} desorption	$O\{a\}(s) \longrightarrow O(g) + (s)$
	LH3 CO{a} desorption	$CO\{a\}(s) \longrightarrow CO(g) + (s)$
	LH3 CO{b} desorption	$CO\{b\}(s) \longrightarrow CO(g) + (s)$

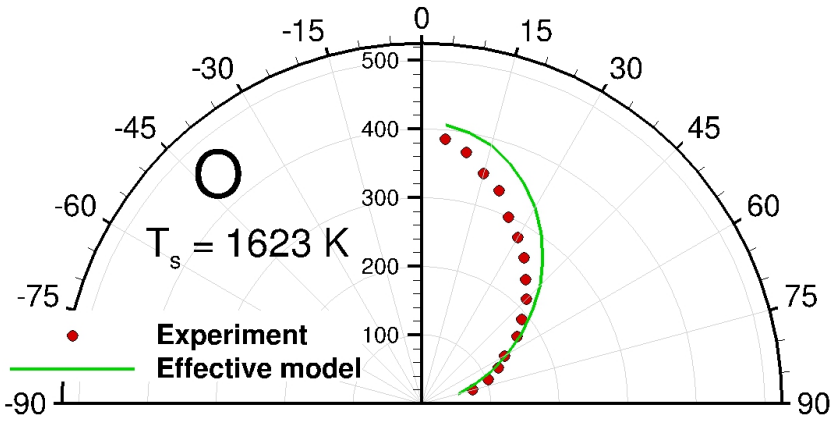


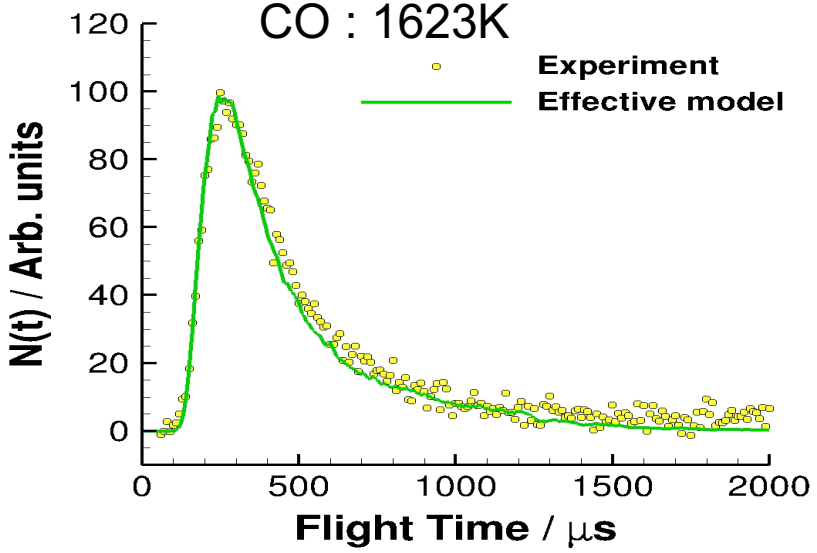
Effective model for use in CFD

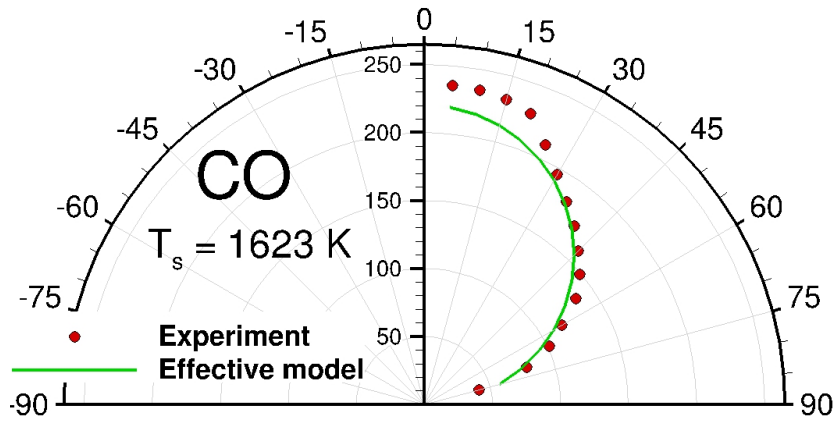
Type	Mechanisms	Reaction	Rate constant (k)
Adsorption	Adsorption	$O(g) + (s) \longrightarrow O(ads)$	$\frac{1}{\Phi} * \frac{1}{4}\sqrt{\frac{8k_bT_g}{\pi m}} * 0.892$
GS reactions	LH1 O formation	$O(ads) \longrightarrow O(TD)(g) + (s)$	$7.85\ exp(-\frac{5154.6}{T_s})$
	LH1 CO formation	$O(ads) + C(b) + O'(ads) \longrightarrow CO(g) + (s) + O'(ads)$	$\frac{1}{\Phi} * 964555.3\ exp(-\frac{16574.0}{T_s})$
	LH3 O{a} formation	$O(ads) \longrightarrow O\{a\}(s)$	1
	LH3 CO{a} formation	$O(ads) + C(b) + O'(ads) \longrightarrow CO\{a\}(s) + O'(ads)$	$\frac{1}{\Phi} * 8337.8\ exp(-\frac{10360.8}{T_s})$
	LH3 CO{b} formation	$O(ads) + C(b) + O'(ads) \longrightarrow CO\{b\}(s) + O'(ads)$	$\frac{1}{\Phi} * 57.83\ exp(-\frac{2908.9}{T_s})$
PS reactions	LH3 O{a} desorption	$O\{a\}(s) \longrightarrow O(g) + (s)$	$0.05\ T^2\ exp\left(-\frac{3177.2}{T_s}\right)$
	LH3 CO{a} desorption	$CO\{a\}(s) \longrightarrow CO(g) + (s)$	$4485.5\ exp\left(-\frac{1581.4}{T_s}\right)$
	LH3 CO{b} desorption	$CO\{b\}(s) \longrightarrow CO(g) + (s)$	$1.2\ exp\left(-\frac{2251.6}{T_s}\right)$

Effective model for use in CFD



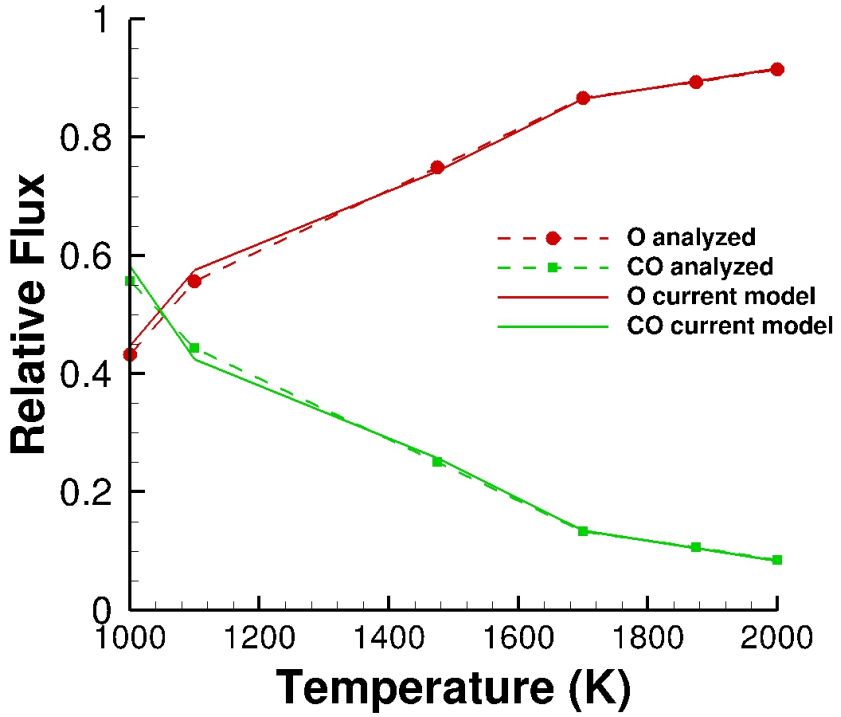




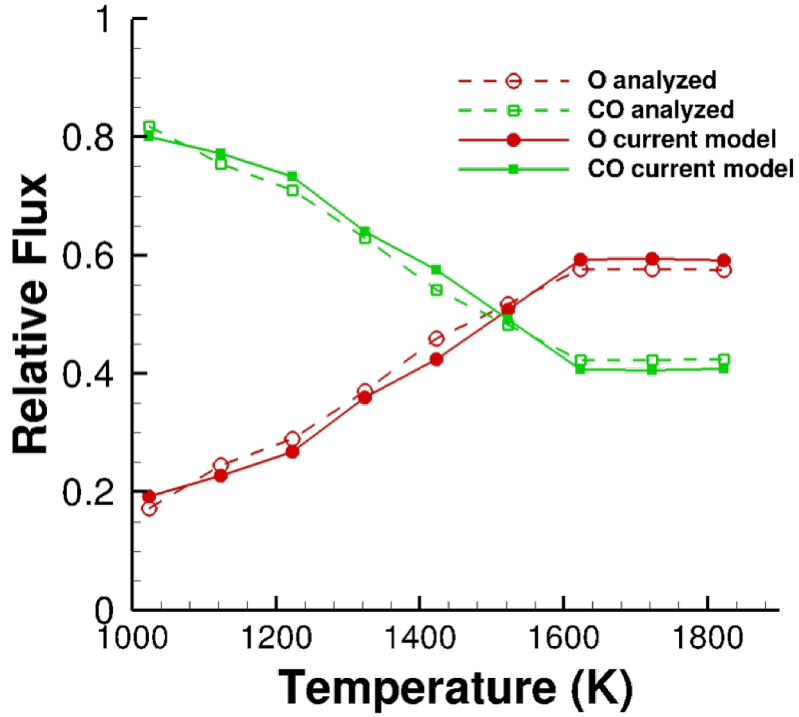


Vitreous Carbon and Effective model

Vitreous Carbon model



Effective model



FiberForm – Varying Porosity

Varying porosity

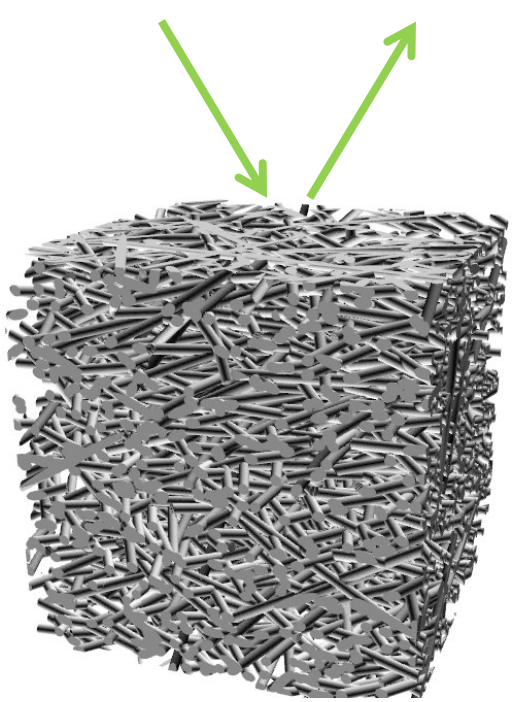
ϕ = 0.84

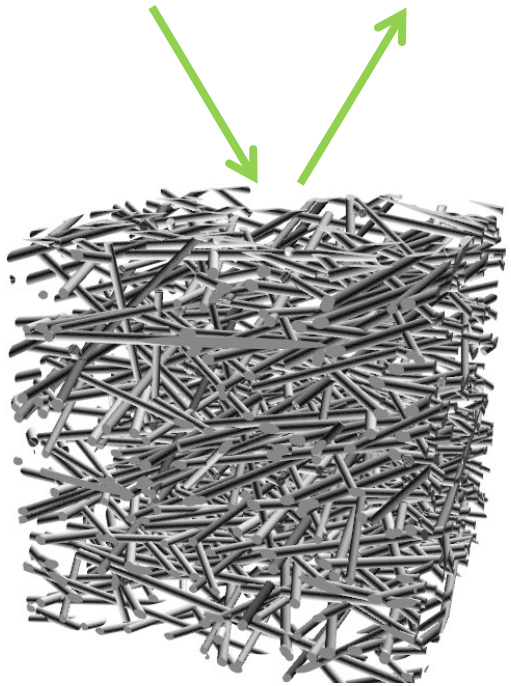
ϕ= 0.90

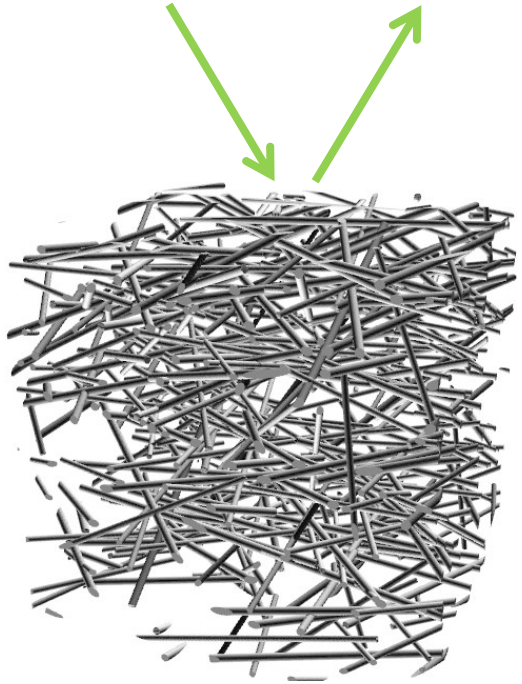
ϕ = 0.96

FiberForm – Varying Porosity

Real model Rates → k







Effective Rates → $k_{eff}(T)$

Effective Rates → $k_{eff}(T)$

Effective Rates → $k_{eff}(T)$

Effective model Rates → $k_{eff}(T,\phi)$

FiberForm – Varying Porosity

Mechanisms	Reaction	Rate constant $k = f(\Phi) * A * exp(-E/T)$				
		$f(\Phi)$	$A = a_0 + a_1 * \epsilon^1 + a_2 * \epsilon^2$			E
			a_0	a_1	a_2	
Adsorption	$O(g) + (s) \longrightarrow O(ads)$	$\frac{1}{\Phi} * \frac{1}{4}\sqrt{\frac{8k_bT_g}{\pi m}}$	+1.335E−1	+1.583E+0	−8.177E−1	0
LH3 O{a} formation	$O(ads) \longrightarrow O\{a\}(s)$	1	1	0	0	0
LH3 CO{a} formation	$O(ads) + C(b) + O'(ads) \longrightarrow CO\{a\}(s) + O'(ads)$	$\frac{1}{\Phi}$	−7.343E+4	+1.636E+5	−7.997E+4	+1.036E+4
LH3 CO{b} formation	$O(ads) + C(b) + O'(ads) \longrightarrow CO\{b\}(s) + O'(ads)$	$\frac{1}{\Phi}$	−5.093E+2	+1.134E+3	−5.547E+2	+2.909E+3
LH1 O formation	$O(ads) \longrightarrow O(TD)(g) + (s)$	1	+6.298E+1	−1.151E+2	+5.943E+1	+6.155E+3
LH1 CO formation	$O(ads)+C(b)+O'(ads) \longrightarrow CO(g)+(s)+O'(ads)$	$\frac{1}{\Phi}$	−8.495E+6	+1.892E+7	−9.251E+6	+1.657E+4

Summary

Conclusions

- Detailed surface chemistry framework was implemented in PuMA.
- The vitreous carbon (VC) model was extended to FiberForm® and validated.
- Effective oxidation model as a function of structural properties and temperature k_{eff} (T,Φ) was developed for use in CFD.

Future Work

- Extension to other species (N)